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L4: Entry 1 of 1 File: DWPI May 22, 1974

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TITLE: Paper-coating copolymer compsn - contg two acrylic ester copolymers, giving lowe viscosity and high shear resistance

PRIORITY-DATA: 1966DE-B086570 (April 7, 1966), 1966DE-B088457 (August 12, 1966)

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ABSTRACTED-PUB-NO: DE 1696163B
BASIC-ABSTRACT:

A paper-coating compsn. contains, per 100 pts. wt. finely-divided pigment, 1-25 pts. binder, which is a mixt. of 90-99.5 (94-98) wt. % of (A) a copolymer with glass temp. between -60 and +30 degrees C (-30 degrees C to +10 degrees C) of 20-70 (30-50) wt. % styrene (pref.) and/or acrylonitrile, 80-30 (70-50)% (meth)acrylic esters of 1-12C alkanols, and possibly is not >10% of another ethylenically unsatd. cpd., and 10-0.5 (6-2) wt. % of (B) an alkali-sol. copolymer with K value 12-40, of 60-95 (70-90) wt. % (meth)acrylic esters of 1-8C alkanols, 5-40 (10-30)% 3-5C ethylenically unsatd. carboxylic acids, possibly is not >10% (meth)acrylamide and possibly is not >10 wt. % other ethylenically unsatd. cpds. The compsn. has a lower viscosity than known paper-coating compsns., making rapid application possible. The mixt. has high shear stability, uniform flow and good water-resistance, and gives a smooth finish. The compsn. may be used with natural binders, e.g. starch, casein or soya protein. High-quality paper with good printing properties is obtd.

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw De

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(54)	Title:	Paper-coating Compositions *Papierstreichmassen*
(71)	Applicant:	Badische Anilin- & Soda-Fabrik AG.
(72)	Inventor:	Spoor, Herbert, et al.

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BADISCHE ANILIN- & SODA-FABRIK AG

Our reference number [= O.Z.]: O.Z. 24 191 W/La/Gz

Ludwigshafen am Rhein, April 6, 1966

Dr. Expl.

Paper-coating Compositions

The invention relates to paper-coating compositions for the manufacture of printing paper. It relates in particular to the type of synthetic binder contained in the paper-coating compositions.

Although these binders are present in minor amounts, generally 5 to 30% by weight of the amount of pigment, in the paper-coating compositions they largely determine their processing properties and the quality of the coated paper. The paper-coating compositions must be stable in the conventional application process, in roll coating as well, and not to have a tendency to form deposits, e.g., on the roller. At the high operating speeds of modern high-performance coating processes in the paper industry, a high solids content in the coating compositions is necessary, so that the plant's drying capacity is sufficient. Moreover, the paper-coating compositions should have the best possible flow properties, be stable to mechanical stress, such as shear stress, and possess a good pigment-binding capacity.

The use of aqueous dispersions of acrylic ester copolymers as synthetic binders alone or together with natural binders, such as starch, casein, or soybean protein, has been known for a rather long time. They often exhibit insufficient shear stability on high-speed coating machines, and unsatisfactory compatibility with certain pigments, such as satin white. In addition, in starch coating compositions, which contain these synthetic binders, the viscosity of the coating compositions is undesirably high. It is further known from US Patent No. 3 081 198 and Belgian Patent No. 655 981 to use mixtures of acrylic ester copolymers and vinyl ester copolymers with

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acrylic acid–acrylic ester copolymers as synthetic binders for paper-coating compositions. Although coated paper with superior properties is obtained with these paper-coating compositions, the alkaline paper-coating compositions prepared therewith are frequently highly viscous, however, with their viscosity increasing with increased addition of acrylic acid copolymers.

It has now been found that paper-coating compositions containing per 100 parts by weight of finely divided pigment, 1 to 25 parts of a synthetic binder, which is a mixture of an acrylic ester copolymer and/or methacrylic ester copolymer A with a glass transition temperature between -60 and +30°C and a water-soluble ammonium salt, amine salt, or alkali salt of a copolymer B of acrylic esters and/or methacrylic esters with ethylenically unsaturated carboxylic acids having 3 to 5 carbon atoms and optionally natural binders and/or conventional additives possess especially advantageous properties, if they contain as copolymers A, copolymers of

20 to 70% by weight of styrene and/or acrylonitrile,

80 to 30% by weight of esters of monohydric aliphatic alcohols having 1 to 12 carbon atoms and acrylic acid and/or methacrylic acid,

0 to 10% by weight of other ethylenically unsaturated compounds,

and

as copolymers B alkali-soluble copolymers, having K values between 12 and 40, of

60 to 95% by weight of esters of monohydric aliphatic alcohols having 1 to 8 carbon atoms and acrylic acid and/or methacrylic acid,

5 to 40% by weight of ethylenically unsaturated carboxylic acids having 3 to 5 carbon atoms,

0 to 10% by weight of acrylamide and/or methacrylamide, and

0 to 10% by weight of other ethylenically unsaturated compounds,

in amounts of 90 to 99.5% by weight of copolymer A and 0.5 to 10% by weight of copolymer B, based on the sum of these copolymers.

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The synthetic binder mixture, contained in the paper-coating compositions, is especially suitable for joint use with natural binders, such as starch, casein, or soybean protein. Preferably, starch is used as the natural binder. The natural products can also be replaced totally or partially by synthetic binders, which are different from the copolymers A and B to be used as taught by the invention.

In combination with a natural binder, amounts of 1 to 15 parts by weight, preferably 3 to 12 parts by weight, of the mixture of copolymers A and B per 100 parts of pigment can be used. In the absence of a natural binder, 5 to 25 parts by weight, preferably 7 to 15 parts by weight, of the synthetic binder mixture, based on 100 parts by weight of pigment, are used. The entire binder amount should be between 5 and 30 parts by weight, preferably between 7 and 25 parts by weight, based on 100 parts of pigment.

Copolymer A to be used in the copolymer mixture as taught by the invention should contain internally polymerized, in addition to 20 to 70 and particularly 30 to 50% by weight of styrene and/or acrylonitrile, with styrene being preferred, 80 to 30 and particularly 70 to 50% by weight of esters of acrylic acid and/or methacrylic acid. Ethyl acrylate, n-butyl acrylate, isobutyl acrylate, n-hexyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, n-dodecyl acrylate, and the corresponding methacrylates, of which n-butyl acrylate, isobutyl acrylate, and 2-ethylhexyl acrylate are preferred, are mentioned as esters of these acids with monohydric aliphatic alcohols having 1 to 12 and particularly 2 to 8 carbon atoms.

Conventional comonomers, primarily vinyl acetate, vinyl propionate, butadiene, maleic acid dialkyl esters and fumaric acid dialkyl esters, vinyl chloride, or vinylidene chloride, may be used as other ethylenically unsaturated compounds, which may participate in the synthesis of copolymer A in amounts of 0 to 10% by weight. Preferably, the polymer contains internally polymerized 0.1 to 10 and particularly 0.5 to 5% by weight of hydrophilic polar monomers, such

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as ethylenically unsaturated carboxylic acids having 3 to 5 carbon atoms and/or their amides, mono- and di-N-alkylamides, N-methylolamides, or etherified N-methylolamides, e.g., acrylic acid, methacrylic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid, acrylamide, N-methylol methacrylamide, or maleic acid amide, maleic acid diamide, or itaconic acid half-esters. Especially suitable monomers of this type are acrylic acid, methacrylic acid, acrylamide and methacrylamide. It is naturally also possible to use mixtures of the monomers mentioned in the polymerization.

The composition of the monomer mixture, which is used to prepare copolymer A, is limited by the following condition: the glass transition temperature of polymer A should be between -60°C and +30°C, preferably between -30°C and +10°C. The glass transition temperature is understood to be the temperature at which the polymer changes from the vitreous solidified to the rubber-elastic or plastic flowing state. It is the temperature at which upon application of the specific volume the resulting curve has a knee as a function of temperature. Reference is made to the book by L. E. Nielson, *Mechanical Properties of Polymers*, Reinhold Publishing Corp., New York, 1962, p. 11ff, for more detailed information on the glass transition temperature.

All polymers that do not meet the stated condition are not suitable for the binder of the invention. Thus, e.g., a copolymer of 60% by weight of styrene, 38% by weight of tert-butyl acrylate, and 2% by weight of acrylic acid has a glass temperature above 30°C and is therefore unsuitable as a possible copolymer A. In contrast, highly suitable and preferred are copolymers A of 40 to 60% by weight of acrylic acid-n-butyl ester and/or acrylic acid-isobutyl ester, 60 to 40% by weight of styrene, 1 to 5% by weight of acrylic acid and/or methacrylic acid, and 0.5 to 5% by weight of acrylic acid amide or methacrylic acid amide.

Copolymers A are preferably prepared by polymerization of the monomers in aqueous emulsion by conventional methods, primarily with a gradual monomer feed and with use of conventional anionic and/or nonionogenic emulsifiers. Suitable emulsifiers are, e.g., potassium n-

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dodecylsulfonate, sodium isooctylbenzenesulfonate, a p-isooctylphenol reacted with 20 to 30 mol of ethylene oxide, or sodium laurate, which is used in amounts from about 0.5 to 5% by weight, based on the monomers. Conventional radical-forming compounds, such as peroxides, persulfates, or azo compounds, e.g., potassium persulfate, cumene hydroperoxide, or azodiisobutyric acid diamide, can be used as polymerization initiators in this case in amounts between about 0.02 and 2% by weight, based on the monomers. The polymerization temperatures, which are used in the preparation of the copolymers, are generally within the conventional range, i.e., between about 50 and 90°C. They can be lower if redox catalysts or activated initiator systems, e.g., a system of potassium persulfate and ascorbic acid, sodium hydroxymethanesulfinate, or triethanolamine, are used. The dispersions are preferably prepared in concentrations from 20 to 60% by weight of solids content.

Copolymers B according to the invention should be alkali-soluble copolymers, having K values between 12 and 40, of 60 to 90 and particularly 70 to 90% by weight of an ester of acrylic acid and/or methacrylic acid and 5 to 40, particularly 10 to 30% by weight, of ethylenically unsaturated carboxylic acids having 3 to 5 carbon atoms. For example, methyl methacrylate, ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, and n-octyl acrylate may be used as esters of acrylic acid and/or methacrylic acid with monohydric aliphatic alcohols having 1 to 8 and particularly 2 to 4 carbon atoms. Preferred are methyl acrylate, ethyl acrylate, isobutyl acrylate, n-butyl methacrylate, and very especially n-butyl acrylate. Of the ethylenically unsaturated carboxylic acids having 3 to 5 carbon atoms, such as maleic acid, fumaric acid, and itaconic acid, acrylic acid and methacrylic acid are especially suitable. It is also possible to use mixtures of the said monomers in the preparation of the copolymers. The preferred copolymers B contain internally polymerized, in addition to the said types of monomers, up to 10 and particularly 2 to 6% by weight of acrylamide and/or methacrylamide. It is further possible by using up to 10% by weight of monomer units of other typical monomers, such as styrene, acrylonitrile or vinyl acetate, to vary the properties of the copolymers within a narrow range and, if desired, to adjust to special requirements for coating compositions or coated paper.

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Copolymers B can be prepared in a conventional manner by emulsion polymerization or solution polymerization. Preferred are copolymers B that are prepared by polymerization of the monomers in organic solvents that dissolve the monomers and copolymers, particularly in aliphatic alcohols such as ethanol, propanol, or butanol. The solvents can be removed by distillation and the copolymers B can be converted to their aqueous solutions after neutralization with ammonia or other bases. Suitable radical formers for the preparation of the solution polymers are, e.g., benzoyl peroxide, lauroyl peroxide, or azodiisobutyronitrile. The polymerization temperatures are generally between 60°C and the boiling point of the employed solvent. For regulating the molecular weight, i.e., to achieve the indicated K values, conventional chain-transfer agents, such as n-dodecylmercaptan, cyclohexene, or carbon tetrabromide, can also be used in amounts from about 0.05 to 0.5% by weight, based on the monomers, in the preparation of copolymers B. The K values of the copolymers, measured according to H. Fikentscher, *Cellulosechemie*, 13 (1932), p. 58ff, in 1% aqueous solutions, neutralized with ammonia, should lie between 10 and 40 and particularly between 15 and 25.

The paper-coating compositions of the invention contain a mixture of copolymer A and copolymer B. In this regard, the mixture ratio should be selected such that, based on the amount by weight of the sum of copolymers A and B, 90 to 99.5% by weight of copolymer A (solid) is present in addition to 10 to 0.5% by weight of copolymer B (solid) in the finished mixture. Preferably employed copolymer mixtures contain 94 to 98% by weight of copolymer A, in addition to 6 to 2% by weight of copolymer B.

To achieve the desired technical effect, the mixing process can occur before or during the preparation of the coating composition. The order as well in the pooling of components of the coating composition is not significant for the properties of the coating composition or the coated paper. It is advantageous, however, if the aqueous dispersion of copolymer A and copolymer B converted to the aqueous solution are combined in the desired amount ratio before the preparation of the coating composition and the completed mixture is stored. The two polymers

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are namely outstandingly compatible with each other. By admixing copolymer B, in addition, the stability of the dispersion of copolymer A is considerably increased. The most favorable pH value for the mixture is between 6 and 10, whereby ammonia is employed preferably as a base for adjusting the pH.

The polymer mixtures are outstandingly suitable as binders for the preparation of paper-coating compositions, to be specific, as the sole binder, and also preferably together with natural binders, especially with starch. They are combined before coating in a manner known per se with fillers, particularly with clay or titanium oxide, and if necessary with other aids, and neutralized by addition of alkali, e.g., sodium or potassium hydroxide, but preferably ammonia.

The paper-coating compositions of the invention can be applied to crude paper with the use of all known methods. Their particular advantage is in their good rheological properties and in their high shear stability, which makes possible good processing by the technically especially simple roll coating process. They excel further in a uniform flow, good water resistance, and smoothness of the finished coating. These advantageous properties of the coating compositions were not predictable.

In comparison with known paper-coating compositions, which contain, in addition to natural binders, the acrylic ester copolymers alone or in combination with acrylic acid copolymers, the much lower viscosity of the compositions inter alia is to be emphasized (cf. Examples and Comparison Tests), whereby the viscosity declines with increasing additions of copolymer B. The low viscosity allows a very rapid machine processing of the coating compositions to high-quality paper with excellent printing properties.

The parts and percentages cited in the following examples are weight units. The given viscosity values in centipoise (cP) were measured at 20°C with a Brookfield viscometer, 100 rpm.

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The preparation of a dispersion of copolymer A, which is used in Examples 1 to 3, is described below by way of example: in a stirred vessel, 1050 parts of styrene, 1050 parts of acrylic acid-n-butyl ester, 42 parts of acrylic acid, and 10 parts of sodium vinyl sulfonate are emulsified together with 42 parts of an addition product of 25 mol of ethylene oxide to p-isooctylphenol, 84 parts of a similar addition product, which was esterified with sulfuric acid, and 9.6 parts of potassium persulfate in 1960 parts of water. This mixture is introduced into 180 parts of water preheated to 80°C in a polymerization vessel over the course of 4 h at 80 to 85°C with stirring. Next, another 1.5 parts of potassium persulfate in 60 parts of water are added and the reaction mixture is completely polymerized at 85°C. An approximately 50% copolymer dispersion is obtained.

The preparation of a solution of copolymer B occurs particularly using methods common in industry for solution polymerization and is to be described for the copolymers B used in Examples 1 to 3: in a polymerization vessel, 100 parts of isobutanol and 1 part of benzoyl peroxide are heated to about 100°C with stirring and then over the course of about 2 h a mixture of 180 parts of isobutanol, 302 parts of butyl acrylate, 101 parts of acrylic acid, and 17 parts of acrylamide are introduced together with 2 parts of benzoyl peroxide and 0.7 parts of n-dodecyl-mercaptan. The reaction mixture is then kept for 1 h at the same temperature and next the isobutanol is distilled off. The polymer melt, cooled to about 90°C, is neutralized with ammonia water and diluted with water to a solids content of 50%, whereby a clear viscous solution forms. The polymer has a K value of 19.

Examples 1 to 3

To prepare a 64% coating composition, 100 parts of China clay are stirred with a high-speed mixer into a solution of 0.3 parts of tetrasodium pyrophosphate in 43 parts of water. 29.3 parts of a 37.5% dispersion of degraded potato starch in water and 6 parts of the 50% mixture of a dispersion of copolymer A with a solution of copolymer B are added; the coating composition is adjusted to a pH of 8 with sodium hydroxide solution.

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Example 1

The added mixture of copolymers A and B, based on the solids, consists of 96% copolymer A and 4% copolymer B. The resulting coating composition has a viscosity of 8000 cP at 20°C.

Example 2

The added mixture of copolymers A and B, based on the solids, consists of 98% copolymer A and 2% copolymer B. The resulting coating composition has a viscosity of 20,000 cP at 20°C.

Example 3

The added mixture of copolymers A and B, based on the solids, consists of 99% copolymer A and 1% copolymer B. The resulting coating composition has a viscosity of 38,000 cP at 20°C.

Comparison Example for Examples 1 to 3

The coating composition is prepared in the same manner as described in Examples 1 to 3, but 6 parts of a 50% dispersion of copolymer A are added as the synthetic binder; i.e., no copolymer is used. The resulting coating composition has a viscosity of 82,000 cP at 20°C.

Example 4

A 64% starch-containing paper-coating paint is prepared as described in Examples 1 to 3. As the synthetic binder, here, 6 parts of a 50% mixture of copolymers A and B are used. Copolymer A is prepared from 33 parts of styrene, 63.5 parts of n-butyl acrylate, 1.5 parts of acrylic acid, and 2 parts of methacrylamide by the conventional methods of emulsion polymerization. The copolymer B is the copolymer used in Example 1. Copolymers A and B are mixed in a ratio of 97 parts of copolymer A to 3 parts of copolymer B (solid). The viscosity of the resulting coating paint is 12,000 cP at 20°C.

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Comparison Test for Example 4

As stated under Example 4, a starch-containing paper-coating composition is prepared, but 6 parts of a 50% dispersion of copolymer A are added exclusively as the synthetic binder. The viscosity of the resulting coating composition is 75,000 cP at 20°C.

Example 5

As described in Examples 1 to 3, a starch-containing 64% paper-coating composition is prepared. As the synthetic binder, 6 parts of a 50% mixture of copolymers A and B are used. The copolymer A of Example 4 is used as copolymer A, and as copolymer B, a copolymer of 87 parts of ethyl acrylate, 10 parts of acrylic acid, and 1.5 parts of acrylamide having a K value of 23. In the mixture, copolymer A is present in an amount of 97% and copolymer B in an amount of 3%, based on the sum of copolymers A and B. The viscosity of the coating composition is 11,500 cP at 20°C.

Example 6

For the preparation of a casein-containing coating composition, 20 parts of casein are first peptized with 1.1 parts of sodium hydroxide in 78.9 parts of water at 50°C. To 15 parts of a thus prepared casein solution, 100 parts of coating clay and 52 parts of water are introduced batchwise with a high-speed mixer. 24 parts of a 50% mixture of copolymers A and B are added to this mixture.

Copolymer A is prepared by emulsion copolymerization, as described above, from the following monomers: 12 parts of styrene, 18 parts of acrylonitrile, 63.5 parts of n-butyl acrylate, 1 part of acrylic acid, and 0.5 parts of acrylamide. The copolymer described in Example 1 is used as copolymer B. The coating composition is adjusted to a pH of 11 with sodium hydroxide solution and has a viscosity of 1700 cP at 20°C.

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Comparison Test for Example 6

A casein-containing coating composition is prepared as described in Example 6, but used exclusively as the synthetic binder is copolymer A, of which 24 parts of a 50% dispersion are added. The viscosity of the resulting coating composition is 2750 cP.

Example 7

A starch-containing 64% paper-coating composition is prepared as described in Example 1, but with use of the copolymer mixture of Example 6. The viscosity of the coating composition is 9500 cP at 20°C.

Comparison Example for Example 7

If the process is carried out as described in Example 7, but the copolymer dispersion A of Example 6 is used exclusively as the synthetic binder, then the viscosity of the resulting coating composition is 90,000 cP.

Comparison Test 2 for Example 7

The procedure is the same as described in Example 7, but a mixture of 97 parts of the copolymer dispersion A from Example 6 and 3 parts of a solution of a copolymer B having a K value of 75 (measured in cyclohexanone) is used as the synthetic binder. The resulting coating composition has a viscosity of 130,000 cP.

Claim

Paper-coating compositions containing per 100 parts by weight of finely divided pigment 1 to 25 parts of a synthetic binder, which is a mixture of an acrylic ester copolymer and/or methacrylic ester copolymer A with a glass transition temperature between -60 and +30°C and a water-soluble ammonium salt, amine salt, or alkali salt of a copolymer B of acrylic esters and/or methacrylic esters with ethylenically unsaturated carboxylic acids having 3 to 5 carbon atoms

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and optionally natural binders and/or conventional additives, characterized in that they contain, as copolymers A, copolymers of

20 to 70% by weight of styrene and/or acrylonitrile,

80 to 30% by weight of esters of monohydric aliphatic alcohols having 1 to 12 carbon atoms and acrylic acid and/or methacrylic acid,

0 to 10% by weight of other ethylenically unsaturated compounds,

and as copolymers B, alkali-soluble copolymers, having K values between 12 and 40, of

60 to 95% by weight of esters of monohydric aliphatic alcohols having 1 to 8 carbon atoms and acrylic acid and/or methacrylic acid,

5 to 40% by weight of ethylenically unsaturated carboxylic acids having 3 to 5 carbon atoms,

0 to 10% by weight of acrylamide and/or methacrylamide, and

0 to 10% by weight of other ethylenically unsaturated compounds,

in amounts of 90 to 99.5% by weight of copolymer A and 0.5 to 10% by weight of copolymer B, based on the sum of these copolymers.

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